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Zone refining of silver iodide

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Zone refining of silver iodide has been tried under vacuum, iodine and hydriodic acid vapours. It was successful only when silver iodide precipitate was kept under hydriodic acid vapours at 150°C for considerable time. Pinholing with hydriodic acid vapours was found suitable. It was observed that Fe, Mg, Cu, Si and Al all have distribution coefficient $K < 1$. Fe was detected in the forward as well as in the rear end (both in ferric and ferrous states) of the zone refined ingot, though its concentration in the forward end was comparatively much less, thus for Fe, the K value can be taken to be close to unity, may be slightly less than unity.

Introduction

Silver chloride, bromide and iodide as such and their mixed crystals have been extensively used as photographic materials. Moser *et al* (1959) reported that one part in 10^8 of cuprous ion in silver chloride produced a readily detectable change in photolytic behaviour. Burnham *et al* (1960) studied the Hall mobility and ionic conductance of silver halides and reported that these were considerably affected by impurities. Nail *et al* (1957) prepared single crystals of silver halides. Large crystals of silver iodide have not been grown successfully apparently because of the phase transition at 146°C from the high temperature body centred cubic form to the low temperature hexagonal form. Cohen & Dobbenburgh (1928) observed that during this phase change the density of silver iodide decreased remarkably i. e. from 6.009 to 5.865. The cooling crystal thus develops strains cracks. Silver iodide is known to exist in at least six polymorphic modifications. Below 146° and at atmospheric pressure it either exists in cubic sphalerite type α-structure or hexagonal wurtzite β-structure, depending upon the details of the crystallisation process. The crystal structure of silver iodide also changes with pressure. It is also much less sensitive to light and much less transparent in the infra-red than other silver halides. Its high melting point (558.5°C) and low dissociation temperature (522°C) are probable reasons for which much work has not been done on silver iodide crystals, Recently, some heat transfer properties have been studied. Cochrane (1967) has successfully grown single crystals of silver iodide from solution to avoid phase transition. For the present work, zone refining of silver iodide has been carried out as the first step for crystal growing.

Experimental

The experimental operations fall into three parts : (*A*) preparation of silver iodide precipitate, (*B*) pinholing of molten silver iodide through a fine glass capillary, (*C*) zone refining.

A. Preparation of the precipitate

Analytical grade, (Analar) silver nitrate and potassium iodide were taken as starting materials They were dissolved in double distilled water and recrystallised and then dried. All operations were carried out in a dark room with red light. Silver iodide, being the least soluble in water of all the silver halides, has a strong tendency to occultate impurities which are much more difficult to remove from it than other silver halides. The precipitation of silver iodide was done by slowly adding 0.1 M silver nitrate solution with stirring, to an equally dilute ammoniacal solution of potassium iodide until precipitation was complete, then adding nitric acid 1% by volume to prevent peptization. Very fine precipitate, light yellow in colour was formed. It was kept overnight to settle down and the water at the top was decanted the next day.

The precipitate settled at the bottom of the vessel was mixed with water containing 1% nitric acid by volume and kept overnight. The water at the top was again decanted. The precipitate was washed for five times in the same way. Finally the precipitate was filtered through filter paper (Whatman No.42) and washed with plain double distilled water. Water was sparingly used in the final washing as silver iodide has strong tendency to peptize. It was observed that a little part of the precipitate had gone in the colloidal form and passed through the filter paper. Light yellow precipitate in fine powder form was obtained. It was kept in a clean, dry glass dish, covered with black paper and put in an oven maintained at 70°C for drying,

B. Pinholing of molten silver halide

Melting the precipitate and then filtering the molten iodide through a fine glass capillary under some protective atmosphere and passing iodine or hydrogen iodide gas through the material has been termed as pinholing. This practice was first employed by Clark & Mitchell (1956) and later by Gunding (1960) and other workers, mainly for removing scum and water vapour. In recent years, it has become clear that silver halide crystals containing traces of silver oxide have different properties than the purest material. Stasiw & Teltow (1948) established that molten silver halides containing traces of silver oxide have strong tendency to wet glass surface. While cooling, the glass contracts but silver iodide expands, as a result the glass container invariably breaks. The pinholing

serves dual purpose, it disposes of some impurities from the melt in the form of scum, as well as renders the halide workable using glass vessels.

The procedure adopted for pinholing differed slightly from that of Clark & Mitchell (1956). Dry precipitate of silver iodide was introduced through the open end of a 10 cm long pyrex glass tube having 3 cm diameter, the other end of which was connected to a small piece of pyrex glass capillary having 0.5mm diameter. The end of the capillary was connected to another pyrex glass tube of 2.5 cm diameter and about 30 cm in length. The open end through which the precipitate was introduced inside was then sealed. The apparatus was coupled to a two stage vacuum pump. The precipitate was thoroughly outgassed and all volatile impurities and water vapour were removed. When a pressure of the order of 10^{3} mm of Hg was obtained, the pinholing apparatus was filled with hydriodic acid vapour at reduced pressure and sealed. The acid vapour was introduced through a glass 'T' which had one stopcock on each side and was connected to vacuum pump, pinholing appratus and a small glass tube containing the acid The whole apparatus was put through coaxially in two nichrome wire heaters, fixed on some insulating sheet and kept in a vertical position, One heater covered the the upper tube while the lower tube was inside the another heater. The temperature of the upper tube containing the silver iodide precipitate was raised to 150°C and maintained for four hours. Warren (1965) adopted similar technique while zone refining alkali halides. Different workers have passed different gases such as nitrogen, helium, halogen acid vapour, or halogen through the molten silver or alkali halides during pinholing. It was observed that with silver iodide, pinholing under vacuum or iodine was not satisfactory. The apparatus broke every time during cooling. Pinholing under hydriodic acid vapour had also failed when the precipitate was melted directly. This was obviously because hydriodic acid vapour dissociated into hydrogen and iodine above 180°C.

By pointing the tip of a gas burner on the capillary, a little portion of the precipitate was melted and as soon as it flowed and entered the capillary, the flame was withdrawn. The capillary was choked. The temperature of the upper tube was then raised to about 580°C and the whole precipitate was melted. The temperature near the capillary being less, the molten halide therefore, could not flow. The halide was kept in the molten state for about 1 hour, so that all the scum could rise to the top of the molten halide. Temperature near the capillary was raised

and the molten halide was allowed to trickle down drop by drop. When some molten material came down in the lower tube, further trickling stopped, as the pressure in upper and lower tubes, became equal. The lower tube was then heated by means of the lower heater and some of the acid vapour was allowed to bubble through the molten halide. Trickling again started for a while and then stopped. By repeated heating of the lower tube, the molten halide was completely transferred to the lower tube. The scum which consisted of carbonaceous matter, hydrated silica, some unreacted silver oxide and other miscellaneous products was left behind in the upper tube. The apparatus was sealed from the lower end of the capillary. The upper tube and the capillary were discarded. The lower glass tube was employed as the container for zone refining. The pinholed silver halide when solidified was light yellow in colour and was not transparent.

C. Zone refining

Zone refining was carried out by Pfann (1952) for the first time. The subject has been extensively reviewed,, by Pfann (1958) himself and Lark-Horovitz & Johnson (1959). The zone refining apparatus for silver iodide consisted of six nichrome wire heaters, made of 18 SWG wire. Each heater had twelve number of turns. They were connected in series and in a straight line and fixed on a 1.25cm thick insulating board. Each heater was provided with some insulation. Width of each heater was 1.5 cm and these were 5.5 cm apart. The glass tube containing the ingot was passed through these heaters and coupled with a slow moving device. Heaters were kept stationary while the glass container moved. The rear end (where the zones left the ingot) of the glass container was at 4—6° higher level. This type of arrangement has been employed by Moser & Burnham (1961) to avoid matter transport first observed by Pfann (1953). First ten passes were made at 3cm per hour, then the speed was reduced to 1cm per hour. Molten zones about 1.5cm in width were formed. In all 40 zone passes were made.

When zone refining was complete it was observed that colour of the silver iodide ingot varied gradully from one end to the other. This was because of the impurity gradient. The rear end of the ingot was dull yellow. The forward end was somewhat brighter yellow. The glass container was broken and the ingot readily came out, as it did not stick to glass. Silver iodide ingot was granular in nature, it could be easily broken and crushed between fingers. A little portion from each end of the zone refined ingot was taken and subjected to spectrochemical analysis.

Discussion

Fe, Mg,Cu, Si and Al were all found segregated in the rear end of the ingot. The forward end was found to contain Fe, but its concentration was much less than in the rear end. No other impurities were detected in the forward end. This can happen if the distribution coefficient K for Fe is slightly less than unity. Moser *et al* (1961) who studied distribution of specific impurities by adding several ppm of the element to the starting charge of silver chloride and bromide and made 70 passes, found $K > 1$ for Mn, Cd and Ni, and $K < 1$ for Pb but no such impurities were detected in our silver iodide ingot. They also observed $K < 1$ for Cu and Fe which agreed with above observation. Under chlorine atmosphere, they reported $K < 1$, and under vacuum $K > 1$ for Fe in silver chloride. They attributed the reason to Fe being in ferric state in chlorine atmosphere and in ferrous state under vacuum. It is interesting to note that although Cu also undergoes a similar valency change, it does not show similar behaviour. However, silver iodide in which Fe and Cu have $K < 1$ under hydriodic acid vapour, agrees with their results under halogen atmosphere.

Chemical tests could not detect the presence of Fe in the forward end, but the rear end was found to have Fe in both ferrous and ferric states. It can be concluded that K is very slightly less than unity for both ferrous and ferric.

Conclusions

No quantitative measurements were carried out, However it can be concluded from the observations that distribution coefficient $K < 1$ for Fe, Mg, Cu, Si and Al. For Fe the value seems be very near to but definitely less than one. No impurity with $K > 1$ has been observed in silver iodide. The behaviour of silver iodide with respect to impurities is identical to those of silver chloride and bromide.

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